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DEVELOPMENTS IN THE MEASUREMENT OF ACTINIDES AND ^{129}I AT LLNL BY ACCELERATOR MASS SPECTROMETRY

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ABSTRACT

The application of ultra-sensitive heavy isotope measurements continues to expand in a variety of fields relevant to the management of nuclear materials, including nuclear isotope forensics and radiobioassay. We have developed a heavy isotope accelerator mass spectrometry (AMS) system at Lawrence Livermore National Laboratory's (LLNL) Center for Accelerator Mass Spectrometry (CAMS). The system was designed particularly for the measurement of actinide concentrations and isotopic ratios, but also allows the measurement of other heavy isotopes such as ^{129}I . The system includes a fast isotope switching capability that allows flexibility in isotope selection and for the quasi-continuous normalization to a reference isotope spike.

Current background levels for ^{239}Pu and ^{240}Pu are equivalent to $<10^6$ atoms and measurements of known materials indicate that our ^{239}Pu and ^{240}Pu measurements are accurate and precise for samples containing from $\sim 10^{12}$ atoms down to the μBq level ($\sim 10^6$ atoms). Recent exploitation of the fast isotope switching capability has allowed the quasi-simultaneous measurement of several Pu isotopes in individual samples. Our AMS measurement capability has been extended to U isotopes, with particular emphasis on ^{236}U . Our current ^{236}U background level is equivalent to $\sim 10^6$ atoms and the linear measurement range is 5-6 orders of magnitude. We have also utilized our Heavy Isotope AMS system for the measurement of ^{129}I . Initial measurements of available low level samples show that background contributions for 1 mg I samples are below $^{129}\text{I}/^{127}\text{I}$ levels of $\sim 10^{-14}$, and measurements of prepared standard samples demonstrates linear measurement response to $^{129}\text{I}/^{127}\text{I}$ levels greater than 10^{-10} .

The AMS technique provides high rejection of interferences, including molecular interferences, and low susceptibility to matrix components, both of which are of particular relevance to the measurement of complex sample matrices. The attendant significant reductions of demands on sample preparation chemistry allow relatively simple, cost-effective procedures to be employed. When such sample preparation improvements are combined with the high sample throughput capabilities of our AMS system, the result is a rapid and cost-effective measurement technique for heavy isotopes in a wide range of studies.

INTRODUCTION

Accelerator mass spectrometry is an ultra-sensitive technique for the detection of rare isotopes. AMS techniques have been applied with great success to a number of long-lived radioisotopes that have not been routinely measured by decay counting; e.g., ^{10}Be , ^{26}Al , ^{36}Cl and ^{41}Ca . With

the application of AMS to the measurement of such long-lived, rare radioisotopes, 50-100 samples can be measured per day, measurement precisions of better than 10% can be achieved for samples containing $\sim 10^6$ rare isotope atoms, and rare-to-stable isotope ratios can be as low as 10^{-14} – 10^{-16} . The basics of the AMS technique, including aspects of particular relevance to the measurement of actinides, have been described previously; e.g., Brown *et al.* [1], Marchetti *et al.* [2]. Two aspects of the AMS techniques used at LLNL of significance to low-level measurements of heavy isotopes are: 1) the samples are introduced into the measurement system in solid form (generally as 0.1–10 mg of a metallic carrier in addition to the actinide sample of interest in oxide form), and 2) the production of energetic (1–100 MeV) positively charged ions by electron stripping during transit through the accelerator also results in the breakup of molecular species, effectively eliminating the possibility of molecular ion interference.

THE LLNL/CAMS HEAVY-ISOTOPE AMS SYSTEM

The Heavy Isotope AMS system at LLNL was designed with particular emphasis on measurements of actinide concentrations and isotopic ratios. The configuration of the system used for measurements of Pu isotopes is shown in Figure 1 (essentially the same configuration is used for U isotope measurements). This heavy-isotope system is comprised of a heavy-isotope high energy (HE; post-accelerator high energy spectrometer) beamline coupled with an ion source and low-energy (LE; pre-accelerator low energy mass spectrometer) ion transport components. The original hardware portion of this system was supported, in part, by the US DOE Office of Non-Proliferation and National Security (NN-20).

The low energy mass spectrometer section consists of three elements: 1) a Cs sputter negative ion source, 2) a spherical electrode electrostatic analyzer (ESA), and 3) a 90° bend injection magnet. The Cs sputter ion source was designed to produce high intensity negative ion beam suitable for injection into the accelerator. The LE ESA provides sufficient energy resolution to reject high-energy sputter tails before transport to the injection magnet. The injection magnet provides sufficient magnetic rigidity resolution to allow the rejection of $^{238}\text{U}^{16}\text{O}^-$ ions during the injection of $^{239}\text{Pu}^{16}\text{O}^-$ ions.

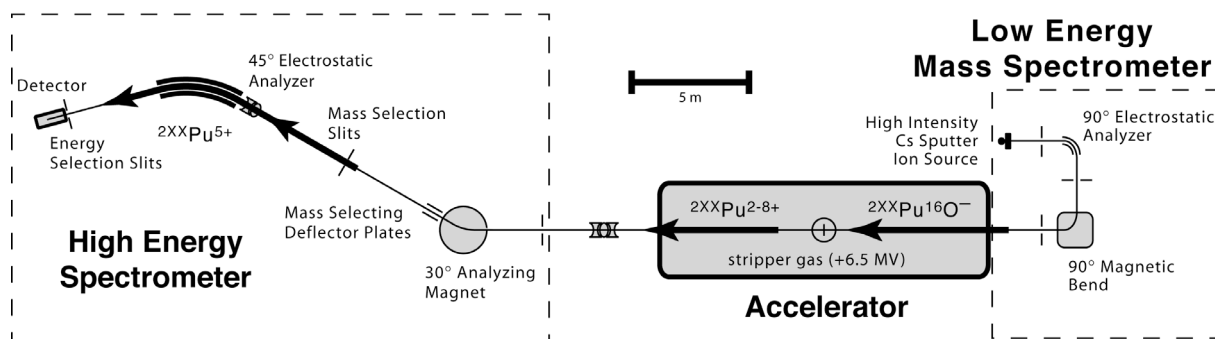


Figure 1. Schematic diagram of the LLNL Heavy Isotope AMS system as used for Pu isotope measurements.

The heavy-isotope HE beamline was designed to transport and filter ions of mass 200-250 at several tens of MeV energies and allow an adequate level of particle detection and identification. The heavy-isotope HE beamline consists of two main beam line elements: 1) a 30° magnetic bend, and 2) a 45° electrostatic bend. The 30° magnetic bend provides sufficient magnetic rigidity resolution to allow 38 MeV $^{239}\text{Pu}^{5+}$ ions to be cleanly separated from 38 MeV $^{238}\text{U}^{5+}$ ions (that may have been injected into the accelerator either as mass peak tails or molecular hydrides). The 45° electrostatic bend is provided by a cylindrical ESA having a 5 cm plate gap, a 4.4 m radius and maximum plate voltages of ± 125 kV. The ESA provides sufficient energy resolution to separate 38 MeV $^{239}\text{Pu}^{5+}$ ions from $^{238}\text{U}^{5+}$ having the same magnetic rigidity as the $^{239}\text{Pu}^{5+}$ ions.

The design considerations for the Heavy Isotope AMS system at LLNL also encompassed our interests in the measurement of other heavy isotopes of relevance in areas such as nuclear isotope forensics, nonproliferation and biomedical applications of AMS. In particular, the system components were selected to allow the measurement of ^{129}I . The configuration of the system for ^{129}I measurements (Figure 2) differs from that routinely used for actinide measurements in that normalization of the counted ^{129}I ions is accomplished by comparison to the stable ^{127}I current (rather than counted ions of an isotopic spike as for our routine actinide measurements).

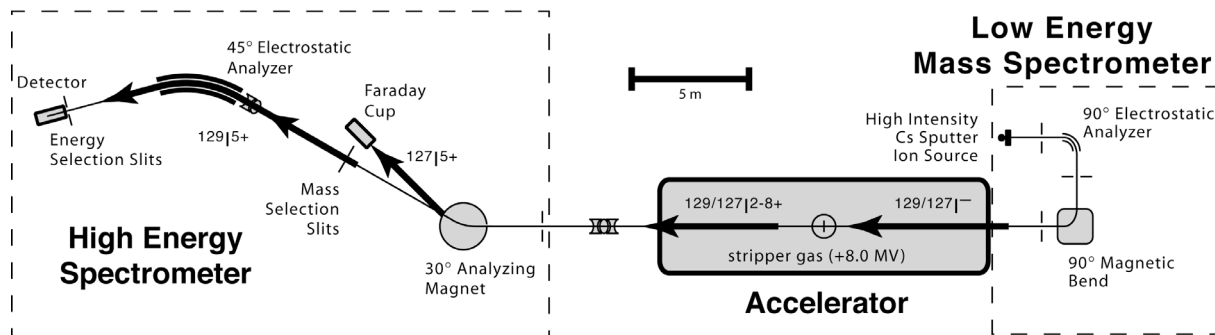


Figure 2. Schematic diagram of the LLNL Heavy Isotope AMS system as used for ^{129}I measurements.

RESULTS

The measurement programs we have undertaken using the Heavy Isotope AMS system have centered on the measurement of Pu and U isotopes in various types of environmental samples, including soils, sediments, waters, and air filters, and on the measurement of samples pertaining to human exposures to Pu and U; e.g., tissue and human urine samples. These programs have included measurements under the US DOE Marshall Islands Program, the US DOD TSWG, and the LLNL Laboratory Directed Research and Development Program. In the past two years of operations we have been able to undertake the optimization of the operating conditions of the Heavy Isotope AMS system for particular U isotopes and ^{129}I , and now undertake routine measurements for Pu isotopes and those U isotopes.

As a part of our efforts towards the development of routine operating conditions and to monitor the performance of our system, we routinely prepare and measure replicate samples derived from a calibrated ^{239}Pu solution (IPL 630-22-3) which span the isotope concentration range of interest for particular studies. Typical results obtained from such a series of replicates are shown in Figure 3. Measurements over the last two years of prepared “Pu blank” samples demonstrate that background levels equivalent to $\leq 3 \times 10^5$ atoms are observed during routine ^{239}Pu and ^{240}Pu measurements. Results obtained from these and similar measurements during a variety of studies also show that the Heavy Isotope AMS system as it is currently operated has a linear measurement dynamic range of greater than 5 orders of magnitude and provides a ^{238}U (molecular ion) interference rejection factor of $>10^7$ during routine ^{239}Pu measurements [3]. The high rejection of ^{238}U interferences implies that environmental samples can be prepared for Pu measurements using relatively routine and simple chemical procedures, which contributes significantly to the establishment of the Heavy Isotope AMS system as a rapid and cost-effective measurement technique for Pu in bioassay and environmental samples.

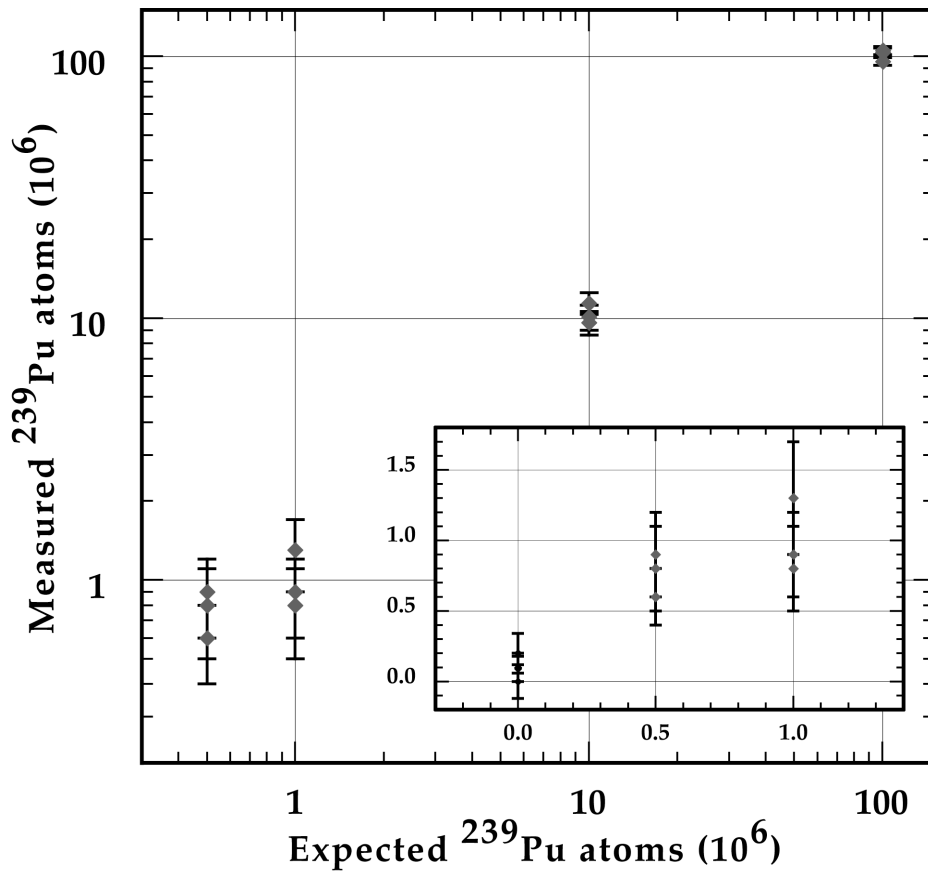


Figure 3. Measurements of samples derived from a calibrated ^{239}Pu solution (IPL 630-22-3) spanning the range from 10^8 atoms to 10^5 atoms. (insert shows lower range on linear scale with blank sample results - blank levels are equivalent to $< 0.3 \mu\text{Bq}$).

Our efforts to evaluate the precision and accuracy of our measurements of Pu isotopes in urine have included blind measurements of a series of NIST prepared synthetic urine samples contained ^{239}Pu , natural uranium and ^{240}Pu . These samples were made available under a DOE Office of International Health supported study that was initiated as part of the ongoing evaluation of the capabilities of various ultra-sensitive methods to analyze ^{239}Pu and ^{240}Pu in urine samples [2,4]. The AMS results obtained for the NIST prepared synthetic urine samples are shown in Figure 4.

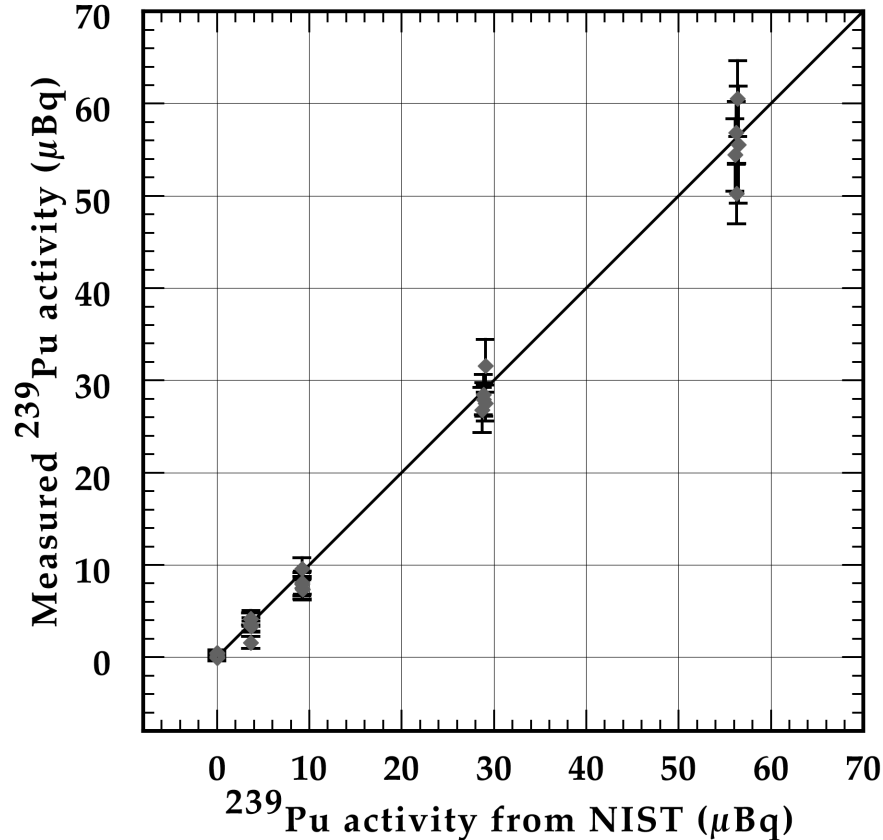


Figure 4. ^{239}Pu activities of NIST supplied synthetic urine samples compared to ^{239}Pu activities derived from AMS measurements of ^{239}Pu contents of samples.

Analyses of the blind measurement results by the study organizers showed that the results for ^{239}Pu and ^{240}Pu obtained at LLNL using the Heavy Isotope AMS system meet ANSI N13.30 and ANSI N42.22 bias, precision and acceptable performance criteria for all samples (^{239}Pu levels extending from 60 μBq to 3 μBq). Significantly, the results showed no evidence of possible ^{238}U interferences on the precision and accuracy of the AMS measurements, demonstrating that the high ^{238}U rejection provided by the Heavy Isotope AMS system allows the use of routine, relatively simple sample preparation chemistry in producing measurements of ^{239}Pu and ^{240}Pu at μBq levels in samples containing significant amounts of ^{238}U .

Over the past two years our efforts have also included the development of the measurement capability for several U isotopes, with emphasis on ^{236}U and ^{233}U . As mentioned above, the configuration of the AMS system for U isotope measurements is essentially identical to that used for Pu isotope measurements. As for our Pu isotope measurements, we routinely prepare and measure replicate samples derived from a calibrated standard, in this case a ^{236}U isotopic standard (IPL 694-79-02). Typical results obtained from such a series of replicates are shown in Figure 5. Measurements over the past year of prepared “U blank” and standard samples demonstrate that background levels equivalent to $\sim 10^6$ atoms are observed during routine ^{236}U and ^{233}U measurements, and that the Heavy Isotope AMS system has a linear measurement dynamic range of greater than 5 orders of magnitude for ^{236}U and ^{233}U measurements.

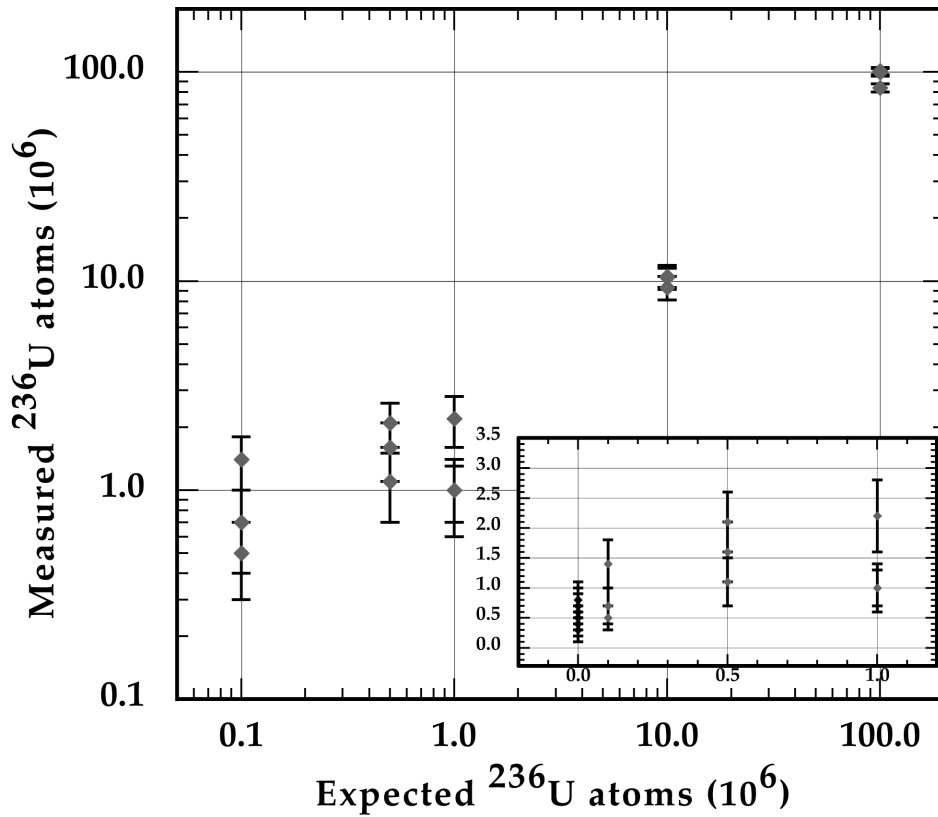


Figure 5. Measurements of samples derived from a calibrated ^{236}U solution (IPL 694-79-02) spanning the range from 10^8 atoms to 10^5 atoms. (insert shows lower range on linear scale with blank sample results - blank levels are equivalent to $<10^6$ atoms).

Over the last year we have also developed an ^{129}I measurement capability using the Heavy Isotope AMS system at LLNL. As mentioned above, for ^{129}I the AMS system is configured slightly differently with the counted ^{129}I ions being normalized to the ^{127}I current measured in an offset Faraday Cup following magnetic mass analysis in the High Energy Spectrometer. To demonstrate the capabilities of our measurement system, we have prepared and measured replicate samples derived from a calibrated standard, in this case an ^{129}I isotopic standard (NIST

SRM 4949C). Results obtained from one such a series of replicates are shown in Figure 6. Measurements over the past year of these samples and prepared “I blank” samples demonstrate that background levels equivalent to $^{129}\text{I}/^{127}\text{I} < 10^{-14}$ are observed under conditions for routine $^{129}\text{I}/^{127}\text{I}$ measurements of samples containing ~ 1 mg I, and that the Heavy Isotope AMS system has a linear $^{129}\text{I}/^{127}\text{I}$ measurement dynamic range of greater than 4 orders of magnitude.

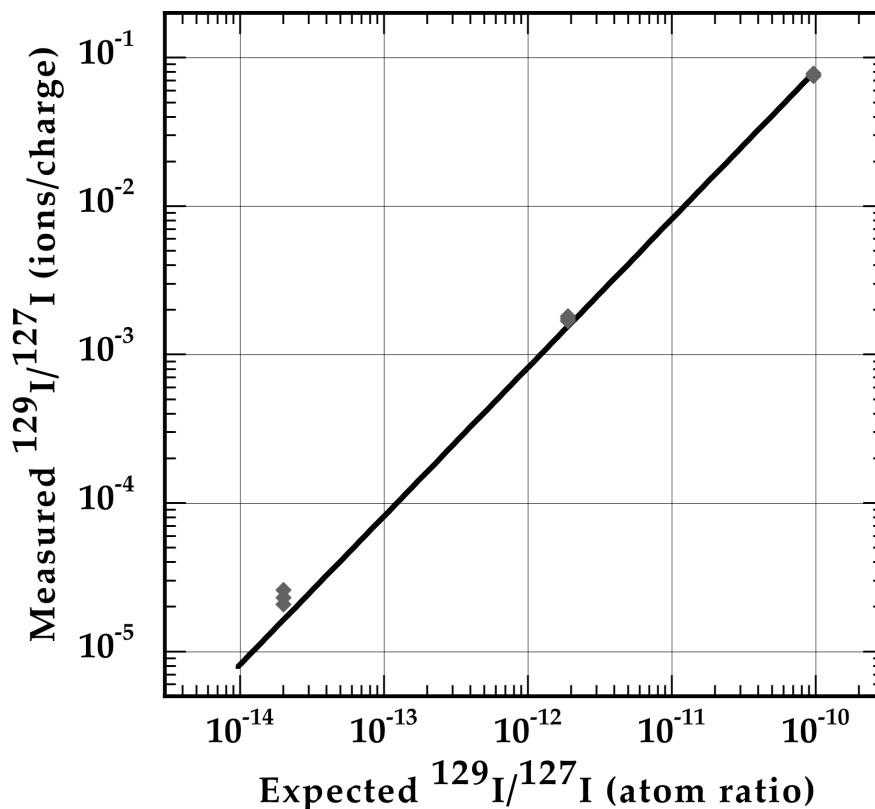


Figure 6. Measurements of samples derived from an ^{129}I isotopic standard (NIST SRM 4949C) spanning the $^{129}\text{I}/^{127}\text{I}$ range from 10^{-10} atoms to $\sim 10^{-14}$.

SUMMARY

We have developed a Heavy Isotope AMS system at the Center for Accelerator Mass Spectrometry at Lawrence Livermore National Laboratory. The system allows rapid and cost-effective measurement of actinide concentrations and isotopic ratios, and of $^{129}\text{I}/^{127}\text{I}$ ratios. In particular, the beamline and data acquisition systems incorporate a fast isotope switching capability that allows quasi-continuous normalization to a reference isotope spike and considerable flexibility in isotope selection.

With the establishment of routine operating conditions for the measurement of Pu and some U isotopes, we have been able to quantify various capabilities of the Heavy Isotope AMS system. Current observed background levels are equivalent to $\leq 10^6$ atoms during routine ^{239}Pu , ^{240}Pu , ^{236}U and ^{233}U measurements. Measurements at ^{239}Pu settings of samples containing 10^{13} ^{238}U

atoms demonstrate that the Heavy Isotope AMS system provides a ^{238}U rejection factor of $>10^7$. Measurements of samples derived from calibrated ^{239}Pu and ^{236}U solutions demonstrate that the measurement system has a linear dynamic measurement range for such isotopes from $\leq 10^6$ atoms to $>10^{11}$ atoms.

For ^{129}I measurements, we have demonstrated that under conditions for routine $^{129}\text{I}/^{127}\text{I}$ measurements for samples containing ~ 1 mg I, background levels equivalent to $^{129}\text{I}/^{127}\text{I} < 10^{-14}$ are observed. And further, that the linear $^{129}\text{I}/^{127}\text{I}$ measurement dynamic range of the Heavy Isotope AMS system is greater than 4 orders of magnitude.

ACKNOWLEDGEMENTS

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